

Thermodynamic assessment of the Bi–Sn–Zn System

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Abstract

A thermodynamic assessment of the Bi–Sn–Zn ternary system was carried out using the CALPHAD approach along with thermodynamic descriptions from new assessments of the Bi–Sn and Bi–Zn systems. Selected experimental data from the literature and our own work were also used. New sets of optimized thermodynamic parameters were obtained that lead to a very good fit between the calculated and experimental data. The Bi–Sn–Zn system is one of the candidates for lead-free solder materials.

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1. Introduction

It is well known that lead and lead-containing materials are toxic and dangerous to the surrounding environment. The EU Directives on Waste Electrical and Electronic Equipment (WEEE) and Restriction of Hazardous Substances (RoHS) prohibited the use of lead in selected electronic equipment sold in the European market. The directives came into force on 13 February 2003, giving 1 July 2006 as the date when the European electronics industry had to be lead-free. Currently, it is generally acknowledged that lead-free soldering is technologically possible (e.g. the Japanese electronics industry is virtually 100% lead-free). Nevertheless, we also have to take into account the adverse properties of possible substituting elements (e.g. toxicity, price, suitability, etc.) in the process of designing new lead-free soldering materials. Selected issues are addressed within the scope of the COST 531 action and the

preparation of a self-consistent thermodynamic database for the alloy systems crucial for lead-free soldering is a major aim of this project.

Following new experimental investigations of the Bi–Sn, Bi–Zn and Bi–Sn–Zn systems, and inconsistencies between assessments of these systems already published, we have found it necessary to reassess their thermodynamic descriptions. The latest version of the SGTE unary database [1] was selected as a basis for the calculations. Phase equilibria studies were carried out in regions of the phase diagrams where the most significant differences exist and the relevant results are also reported in this paper.

This work has contributed significantly to the development of the “COST531” database [2].

2. Theoretical part

The CALPHAD method is used in this work. This procedure is based on the sequential modeling of phase equilibria and thermodynamic properties of alloy systems, starting from binary systems and leading to higher-order systems. It is

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possible to obtain accurate predictions of phase equilibria of multicomponent systems using this approach. The crucial condition for the success of such a method is a good and consistent database for the calculation of the thermodynamic properties of the relevant systems.

The mathematical method for the calculation of thermodynamic equilibrium is based on modeling the Gibbs energies of all phases and minimizing the total Gibbs energy of the system. The total Gibbs energy of the system can be calculated by the formula $G^{\text{tot}} = \sum_p w^p G^p$, where the symbol w^p is the amount of phase p and G^p its Gibbs energy. The Gibbs energy for a particular solution phase is expressed by the general formula $G^p = \sum_i x_i {}^\circ G_i^p + G^{\text{id}} + G^E + G^{\text{mag}} + \dots$, where $x_i {}^\circ G_i^p$ is the contribution of the Gibbs energy of the element i in the crystallographic structure, corresponding to the phase p with respect to its reference state (contribution of the pure components), x_i is the molar fraction of element i , and ${}^\circ G_i^p$ is the molar Gibbs energy of pure element i in the structure, corresponding to the phase p . The symbol G^{id} denotes the ideal mixing contribution; G^E is the contribution due to non-ideal interactions between the components (the excess Gibbs energy of mixing) and G^{mag} is the contribution of magnetic Gibbs energy if the phase exhibits magnetic properties. Other excess Gibbs energy terms can be introduced, e.g. pressure dependence $\{G^{\text{press}}\}$, energy of the interface, energy of plastic deformation, energy of defects in the crystal lattice, etc.

Intermediate phases are usually modeled using the sublattice model [3]. This model is based on the distribution of independent lattice positions in the crystal structure into several sublattices, according to their physical properties. The amount of a particular element in the sublattice k is defined by lattice fractions y_i^k , which are defined as

$$y_i^k = \frac{n_i^k}{\sum_{i=1}^s n_i^k},$$

where n_i^k is number of moles of component i in sublattice k , and s is number of components occupying sublattice k .

A real crystallographic lattice can be envisaged as a superposition of several sublattices from this point of view [3]. The Thermo-Calc software [4] was used in this work for the optimization of the model parameters and calculation of phase equilibria and thermodynamic properties.

3. The Bi–Sn–Zn system and its subsystems

3.1. Introduction

An extensive experimental investigation of the Bi–Sn–Zn system has been conducted by Braga et al. [5]. The solubilities of the components in the terminal solid solutions were measured and compared with predictions using thermodynamic parameters from [6] and [7]. However, discrepancies between experimental and calculated solubilities were found for Bi in HCP_Zn, and particularly for the solubility of Bi in BCT_A5 (Sn). The results given in [5] indicated a much lower solubility

of Bi in the BCT_A5 (Sn) solid solution (around 10 wt% at the eutectic temperature) and confirmed the need for a new thermodynamic description for the Bi–Sn system. This fact is especially important from the point of view of the development of the “COST531” thermodynamic database [2] because other important ternary system descriptions are based on this binary. Therefore, targeted experiments using scanning electron microscopy (SEM) + energy-dispersive solid-state spectrometry (EDS) and differential scanning calorimetry (DSC) were carried out in the Sn-rich part of the Bi–Sn phase diagram as part of the experimental study [5].

Disagreement between the experimental ternary phase equilibria and the solubility limit of bismuth in HCP_Zn calculated using the assessed thermodynamic parameters led to small changes in the description for the Bi–Zn system, too.

Experimental studies and the remodeling of the binary and ternary systems are summarized and discussed in the following sections.

3.2. Bi–Sn system

Many authors have investigated the phase equilibria and thermodynamic properties of this system experimentally, but with a certain amount of disagreement between some of the results. Nagasaki and Fujita [8] measured the specific heat, and Oelsen and Golücke [9] determined heats of mixing. More recently, Ohtani and Ishida [10] reported liquidus data and the eutectic temperature, which they measured using DSC. The agreement among these three sets of data is generally good. Many authors also investigated the enthalpies of mixing of liquid Bi–Sn alloys, e.g. [11–14]. As Ohtani and Ishida [10] pointed out, work carried out before the 1940's (e.g. [11]) show large scatter while there is a rather good agreement amongst later data, e.g. [12–14]. Many authors have measured the activities of Sn in the liquid phase using electromotive force (EMF) methods; one of the most recent works in this field is the contribution of Asryan and Mikula [15]. Yazawa and Koike [16] also measured the activities of Bi in the liquid at 1100 °C, whereas Rickert et al. [17] measured activities at 750–1050 °C. The activities measured by the various authors were in good mutual agreement, showing a slight positive deviation from ideality. However, the calculated enthalpies showed large mutual discrepancies. Only those of Seltz and Dunkerley [18] were in good agreement with directly measured data [12–14]. Enthalpies of formation of solid alloys are also available from the calorimetric measurements made by Oelsen and Golücke [9]. A list of other related references is available in the paper of Lee et al. [19].

Thermodynamic modeling of this system has been carried out by Ohtani and Ishida [10] and Lee et al. [19]. The assessments differ in the unary data used (i.e. the Gibbs energy differences for the pure components in certain crystallographic structure – especially for their metastable states – with respect to Stable Element Reference state of that component). Therefore the phase boundaries calculated using their assessed data disagree. A different solubility of Sn in the Rhombohedral_A7 (Bi) phase can be clearly seen (Fig. 1(a) and

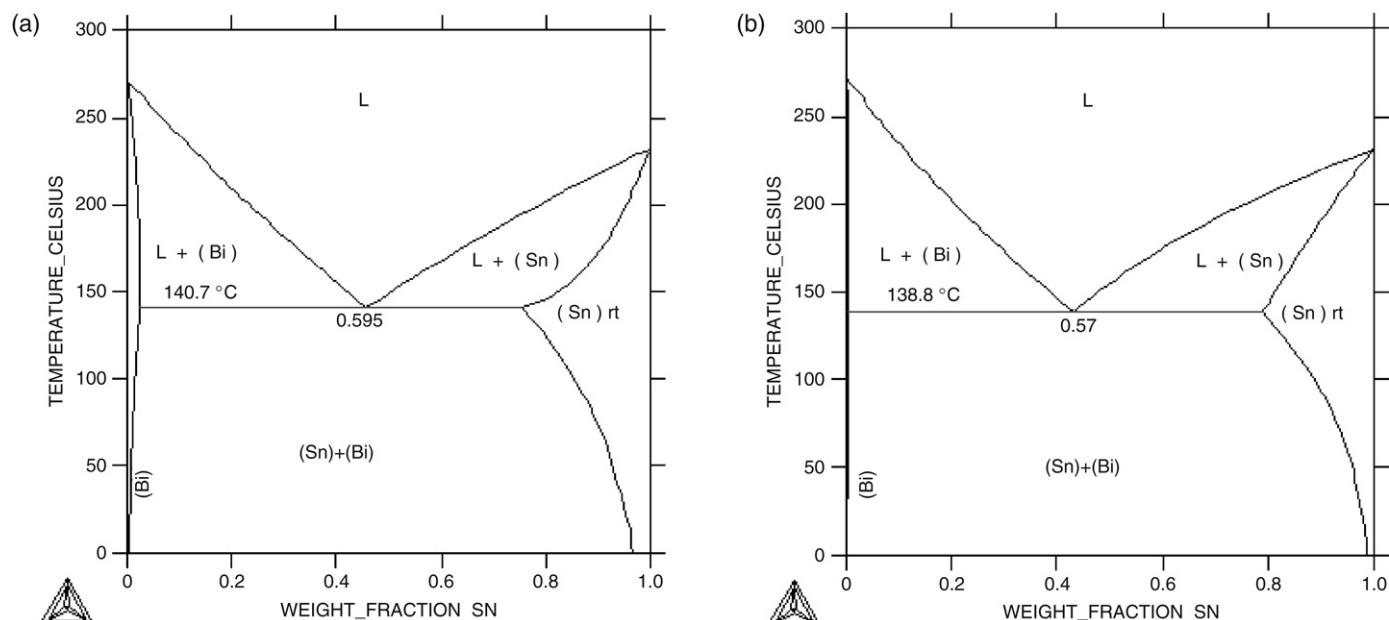


Fig. 1. Optimized phase diagram Bi–Sn according to (a) Ohtani and Ishida [10] and (b) Lee et al. [19].

(b)). Lee et al. [19] did not take into account the solubility of Sn in Rhombohedral_A7 (Bi) reported by Oelsen and Golücke [9] and obtained a much lower solubility in their assessment.

The liquid phase, Rhombohedral_A7 solid solution (Bi-rich) and BCT_A5 solid solution (Sn-rich) are stable in this system. All solid phases were modeled as regular solid solutions with one sublattice.

With respect to the different solubility of Bi in BCT_A5 (Sn-rich) solid solution, we have utilized mainly the newly obtained phase equilibrium data from [5] for the reassessment of the system (Fig. 2 shows these data superimposed on the phase diagram calculated using the thermodynamic parameters from the assessment of Ohtani and Ishida [10]). We have also taken into account new thermodynamic data measured by Asryan and Mikula [15] and the phase equilibrium data published by Oelsen and Golücke [9] concerning the solubility of Sn in the Rhombohedral_A7 (Bi) phase. The selected data of Ohtani and Ishida [10] and Nagasaki and Fujita [8] were used for the comparison with the calculated phase diagram only. We have found that binary thermodynamic parameters published in [10] (using the same unary data for all phases as in our assessment) reproduce reasonable well the phase and thermodynamic data except for the above-mentioned solubility of Bi in BCT_A5 (Sn). Therefore, it seemed reasonable to use the thermodynamic parameters published in their study as starting values in the parametric optimization in this work.

The unary data were taken from v4.4 of the SGTE unary database [1]. The parameters obtained from the present assessment are shown in Table 1. The binary Bi–Sn phase diagram calculated using these newly assessed data is shown in Fig. 3 and is compared with relevant phase equilibrium data taken from our work and those mentioned above. The calculated activity and enthalpy of mixing of liquid Bi–Sn alloys at 450 °C are compared with the calorimetric data of

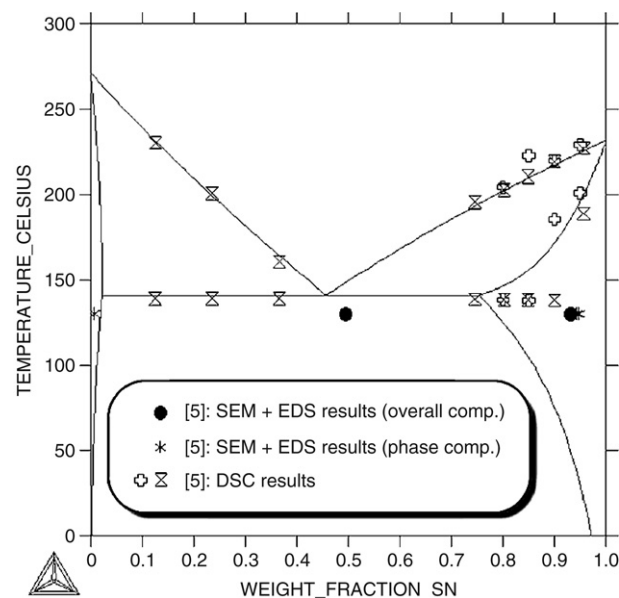


Fig. 2. New experimental data superimposed on the Bi–Sn phase diagram, calculated using the data of Ohtani and Ishida [10].

Sharkey and Pool [14] and Asryan and Mikula [15] in Fig. 4(a) and (b).

3.3. Bi–Zn system

A summary of the experimental data can be found in the papers of Okajima and Sakao [20], Malakhov [21] and Kim and Sanders [22]. Okajima and Sakao [20] studied the equilibria between the two immiscible liquid phases in this system, and the agreement between their experimental data and those of other authors is rather good. Okajima and Sakao [20] also calculated the activities of zinc in the system at 873 K using experimentally determined EMF values and compared them with Kleppa's values [23]. The agreement between the two sets

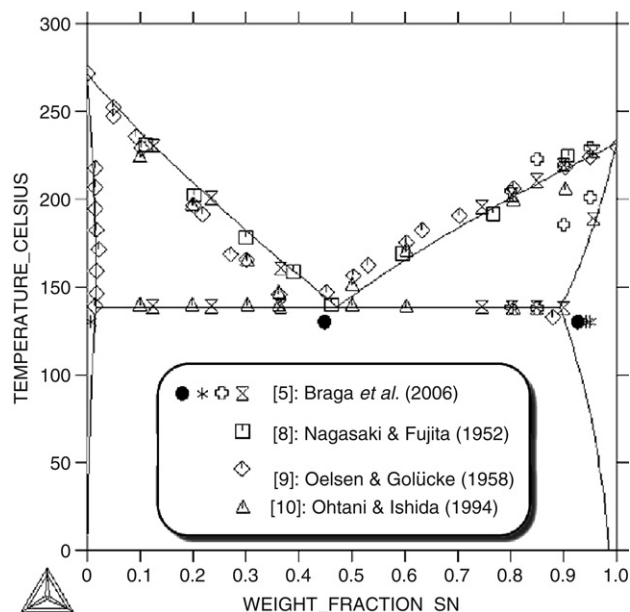


Fig. 3. The assessed Bi–Sn phase diagram in comparison with experimental data used in the assessment.

Table 1
Summary of the thermodynamic parameters of the Bi–Sn system resulting from the present assessment

Phase	Thermodynamic parameters (J mol^{-1})
Liquid	${}^0L_{\text{Bi,Sn}}^{\text{Liq}} = +500.0 + 1.5T$ ${}^1L_{\text{Bi,Sn}}^{\text{Liq}} = -100.0 - 0.135T$
BCT_A5 (Sn)	${}^0L_{\text{Bi,Sn}}^{\text{BCT_A5}} = +3500.0 - 1.038T$ ${}^1L_{\text{Bi,Sn}}^{\text{BCT_A5}} = -3710.0$
Rhombohedral_A7 (Bi)	${}^0L_{\text{Bi,Sn}}^{\text{Rhom_A7}} = +19\,720.0 - 22.60T$ ${}^1L_{\text{Bi,Sn}}^{\text{Rhom_A7}} = -5760.0 + 13.834T$

of data is good. Kawakami [24] and Wittig et al. [25] measured the enthalpies of mixing for liquid alloys.

A thermodynamic assessment of the Bi–Zn system was carried out by Malakhov [21], Oleari et al. [26], Bale et al. [27], Girard [28] and Wang et al. [29]. Recently, Kim and Sanders [22] assessed miscibility gaps and the metastable liquids in this system and published new interaction parameters for the liquid phases. We used the interaction parameters for liquid phases presented by Malakhov [21] in the current work because of better agreement with experimental data and consistency with other data used.

The liquid phase, Rhombohedral_A7 phase (Bi) and HCP phase (Zn) were used in the modeling. The HCP phase (Zn) is of the A3 type, but with a different c/a ratio. Therefore, we modeled it as a different phase (denoted HCP_Zn instead of the standard HCP_A3) in the database. To keep the consistency with other databases, this phase was modeled with two sublattices. The first sublattice is occupied by the metallic elements and the second by interstitial elements, despite the fact that no interstitial elements exist in these systems. The

site-occupancy ratio given by the number of interstitial positions per site on the basic metallic sublattice is 1:0.5.

The currently accepted phase diagrams for the Bi–Zn system are shown in Fig. 5(a) and (b). There is a noticeable difference between the calculated phase diagram according to [21] (Fig. 5(a)) and the assessed experimental phase diagram [30] (Fig. 5(b)).

The assessment published in Massalski's compendium [30], based on existing experimental results, indicates a significant solubility of Zn in Rhombohedral_A7 (Bi) (~ 2 wt% of Zn) but the calculations carried out using Malakhov's data [21] indicated a much lower solubility (significantly less than 1 wt%). The calculations for the Zn-rich end of the phase diagram gave a negligible solubility of Bi in HCP_Zn; less than 0.1 wt%. Experimental results [5] at 245 °C confirmed the low solubility of Zn in Rhombohedral_A7 (Bi), as the sample with a Zn content of approximately 0.3 wt% clearly exhibits a two-phase structure. The solubility of both elements in the respective solid solution was found to be approximately 0.3 wt% at 200 °C. This value is in good agreement with the theoretical calculation for the solubility of Zn in Rhombohedral_A7 (Bi), as the calculated solubility at 200 °C is 0.37 wt% of Zn. On the other hand, the calculation according to Malakhov [21] gives much lower solubility of Bi in HCP_Zn than the experiment result (Fig. 5(a)). The difference is not large in absolute numbers, as the solubility is very low, but the calculated value is about 10 times lower than the experimental result. After analysis of the experimental data, the interaction parameter ${}^0L_{\text{Bi,Zn:Va}}^{\text{HCP_Zn}}$ in the Bi–Zn binary system given by Malakhov [21] was changed from +35 000 to +25 000 J mol^{-1} . The resulting difference in the position of the phase boundary calculated using both parameters can be seen by comparing Fig. 6(a) and (b).

3.4. Sn–Zn system

An overview of the experimental data and an estimation of the phase diagram have been published by Moser et al. [31]. The available experimental data for the liquid covered both the enthalpy of mixing and chemical potentials (or activities) of Zn in the liquid state; the data are in very good agreement with each other. The activity measurements were carried using the EMF method, e.g. by Sano et al. [32] and Fiorani and Valenti [33], or by the vapor pressure method, e.g. by Scheil and Müller [34] and Kozuka et al. [35]. Kleppa [36], Oelsen [37] and Schürmann and Träger [38] measured the enthalpies of mixing.

Thermodynamic modeling of this system has been carried out by Ohtani et al. [39], Lee [40] and also by Fries et al. [41]. They used the temperature dependence of the enthalpy of mixing for the liquid measured by Kleppa [36] and Bourkba et al. [42] for their assessments. The above authors used different unary data in their assessments and there are also differences in the resulting phase boundaries (Fig. 7(a) and (b)), where a different solubility of Zn in BCT_A5 (Sn) is clearly seen. It is difficult to decide which phase diagram is correct, as the available experimental data are limited in this region. The thermodynamic parameters from Fries et al. [41] were used in

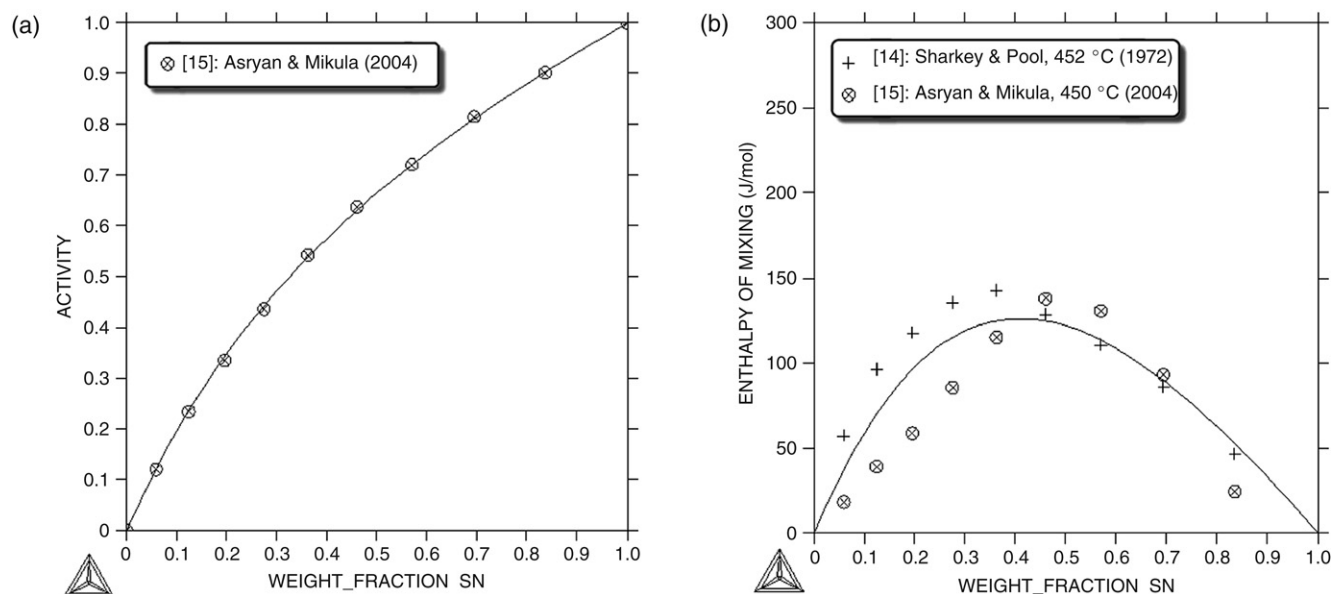


Fig. 4. Calculated (a) activity of Sn and (b) enthalpy of mixing of liquid Bi–Sn alloys at 450 °C in comparison with experimental data used in the assessment.

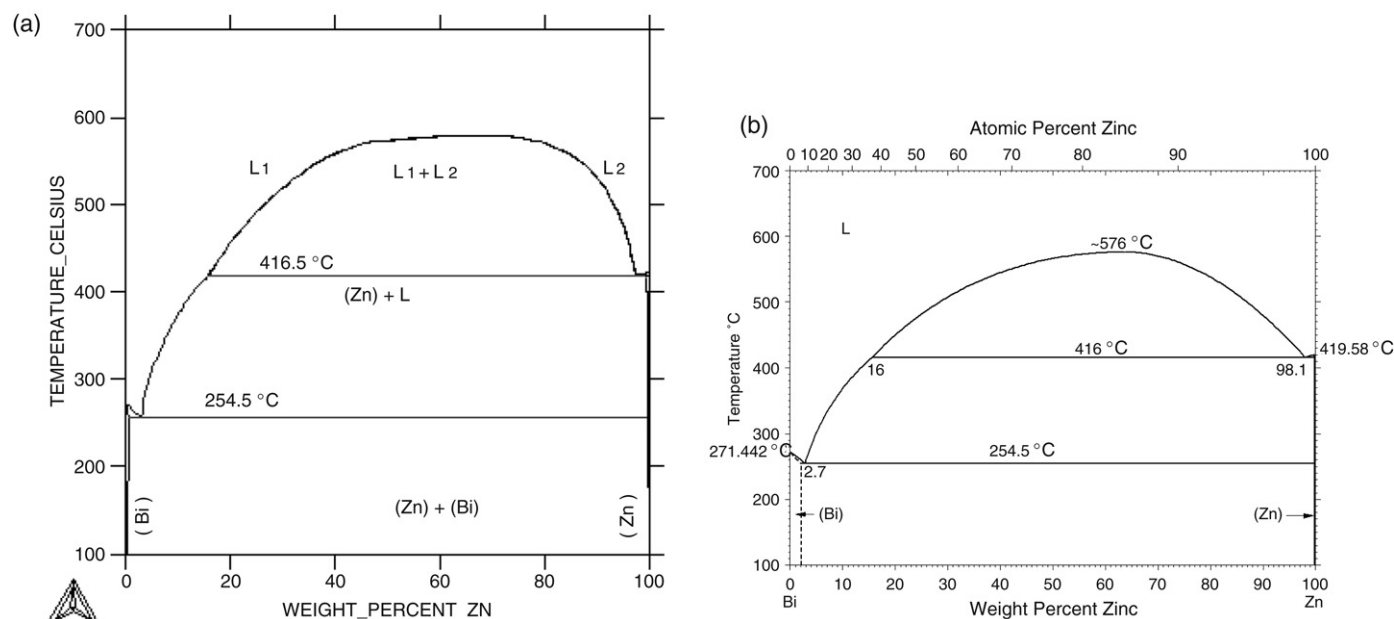


Fig. 5. Calculated Bi–Zn phase diagram using data from Malakhov [21] (a) and assessed experimental Bi–Zn phase diagram from Massalski [30] (b).

the “COST531” database [2] and in our study as they exploited the unary data from the SGTE 4.4 database [1]. The standard state for Sn is BCT_A5; the standard state for Zn is HCP_Zn with the non-standard c/a ratio.

3.5. Bi–Sn–Zn system

The ternary Bi–Sn–Zn system was assessed by Malakhov et al. [6] and Moelans et al. [7]. Both assessments are based on the experimental work of Muzaffar [43], who carried out thermal analysis of a large number of liquid alloys. The experimental information gave a eutectic temperature of $T = 129.87 \pm 0.15$ °C. Malakhov et al. [6] also took into account the results of Ohtani and Ishida [10] and Ohtani et al. [39]. Moelans

et al. [7] used thermochemical properties determined from EMF measurements made by a number of authors, e.g. [27, 44–46]. Both Malakhov et al. and Moelans et al. introduced ternary corrections for the liquid only. Unfortunately, the assessments of this system are not mutually consistent as the authors used different unary data (e.g. $G_{\text{Bi}}^{\text{BCT}_A5} - G_{\text{Bi}}^{\text{Rhom}_A7} = +4184.07 \text{ J mol}^{-1}$ from [10] and $+13526.3 \text{ J mol}^{-1}$ from [19] in the Bi–Sn system). They either took these values from various versions of the SGTE unary database [10,19] or, in some cases, carried out their own assessment of the unary data [7]. Recently, Luef et al. [47] published an experimental study of this ternary system and determined partial and integral enthalpies of mixing of liquid Bi–Sn–Zn alloys at 500 °C by a drop calorimetric technique. Experiments were

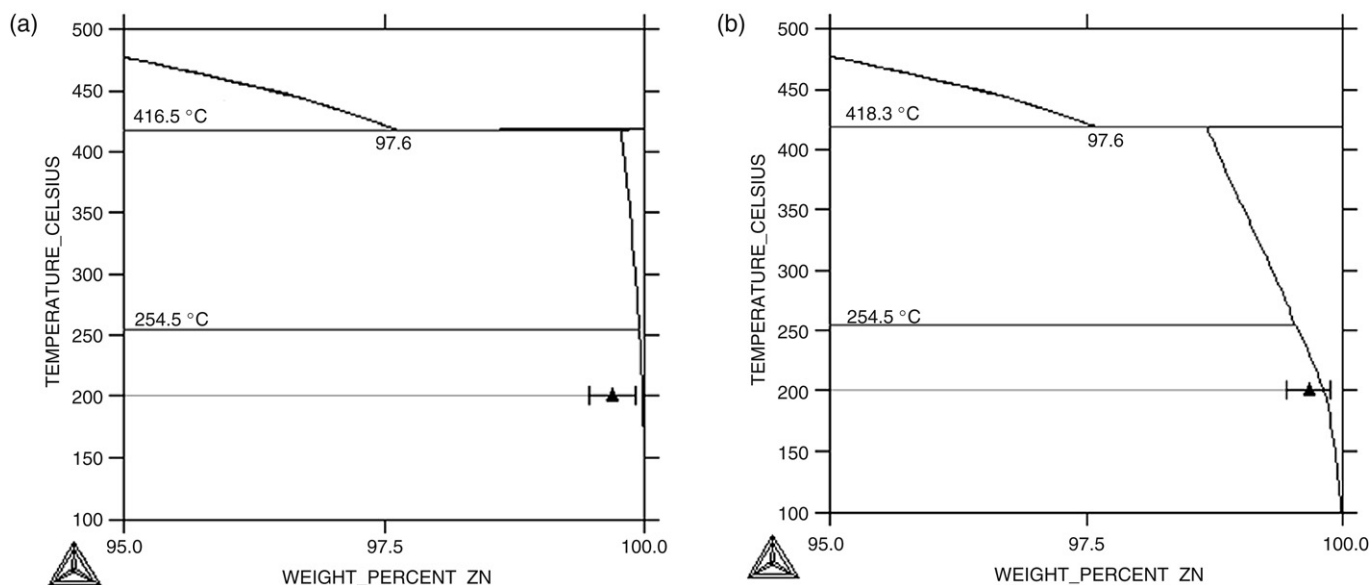


Fig. 6. Calculated Zn-rich part of the Bi–Zn phase diagram, using (a) data from Malakhov [21] (without correction) and (b) data from the “COST531” database [2] (utilizing the interaction parameter correction) in comparison with new experimental results [5].

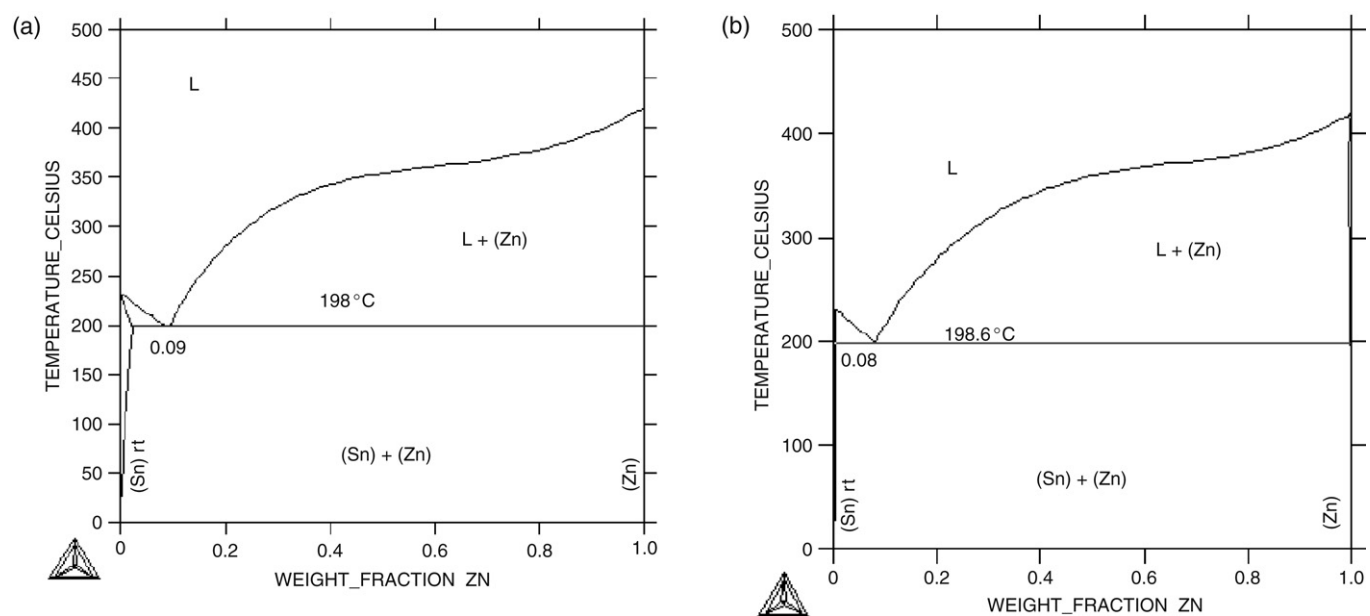


Fig. 7. Optimized Sn–Zn phase diagram according to (a) Ohtani et al. [39] and (b) Fries et al. [41].

conducted using compositions along six sections in the Sn-rich part of the ternary diagram. They also reported DSC data (liquidus temperatures and ternary eutectic reactions) along three sections (3, 5 and 7 at.% of Zn). Braga et al. [5] published new and significant experimental results focusing on the miscibility gap (and also the Sn-rich part of the diagram). DSC, X-ray diffraction (XRD), and SEM in conjunction with EDS were used in the study. For quantitative analysis they used X-ray fluorescence (XRF) and atomic absorption spectrometry (AAS).

Both Malakhov et al. [6] and Moelans et al. [7] have used the older thermodynamic description of the Bi–Sn system for their assessments, and therefore it was necessary to reassess the Bi–Sn–Zn system using the newly assessed Bi–Sn

system (Section 3.2) together with the Bi–Sn–Zn experimental results presented in [5,43]. These experimental data were supplemented with new experimentally determined integral enthalpies of mixing of liquid Bi–Sn–Zn alloys [47] and the activities [45].

Ternary interaction parameters were introduced both for the liquid and Rhombohedral-A7 (Bi) phases modifying the ternary system behavior. No ternary interaction parameters were necessary for the BCT-A5 (Sn) phase, as the predicted solubility of Bi and Zn in this phase agreed well with the experimental results. Using the Parrot module [4] of the Thermo-Calc thermodynamic calculation software, a new set of thermodynamic parameters was optimized for the ternary system, which is summarized in Table 2.

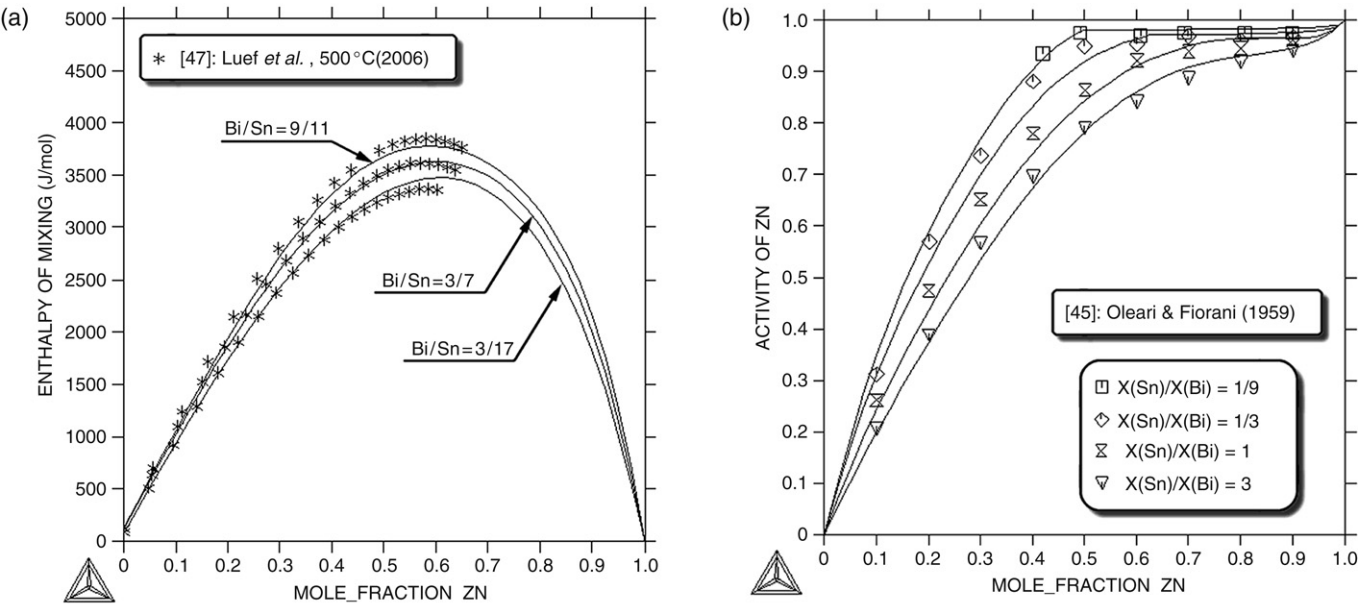


Fig. 8. Calculated (a) integral enthalpies of mixing at 500 °C, compared with the experimental data of Luef et al. [47], and (b) activities of Zn at 450 °C, compared with the experimental data of Oleari and Fiorani [45].

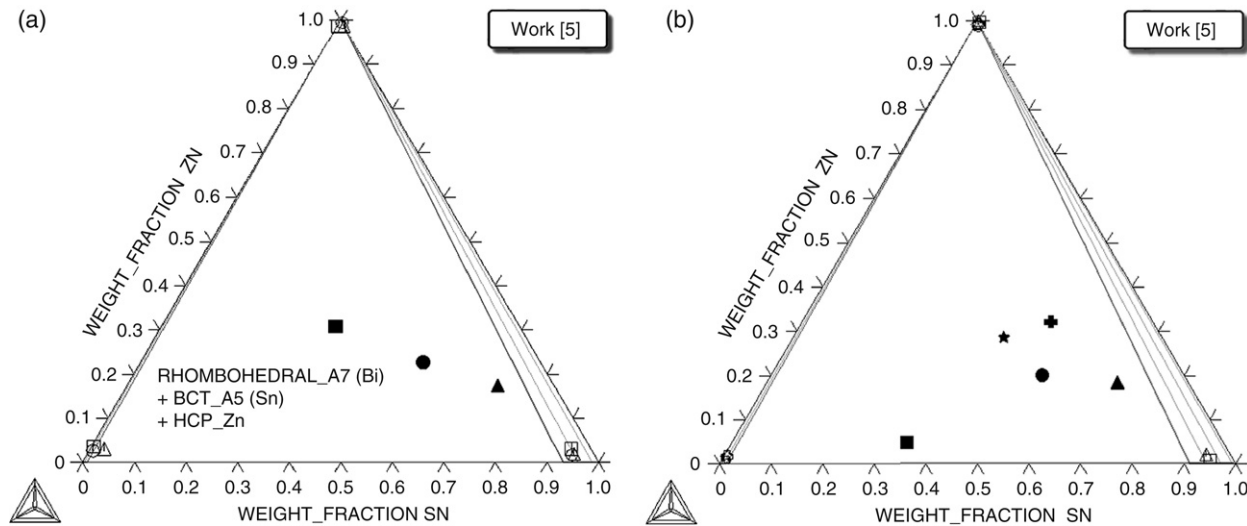


Fig. 9. Calculated isothermal sections at (a) 100 °C and (b) 120 °C in comparison with experimental data from Braga et al. [5].

Table 2
Summary of the ternary corrections for the Bi–Sn–Zn system used in the present assessment

Phase	Thermodynamic parameters (J mol ^{−1})
Liquid	${}^0L_{\text{Bi,Sn,Zn}}^{\text{Liq}} = -17\,690.6 + 33T$ ${}^1L_{\text{Bi,Sn,Zn}}^{\text{Liq}} = -2737.2 - 13T$ ${}^2L_{\text{Bi,Sn,Zn}}^{\text{Liq}} = -19\,259.1 + 0.5T$
Rhombohedral_A7 (Bi)	${}^0L_{\text{Bi,Sn,Zn}}^{\text{Rhom_A7}} = +387\,000.0$ ${}^1L_{\text{Bi,Sn,Zn}}^{\text{Rhom_A7}} = 0$ ${}^2L_{\text{Bi,Sn,Zn}}^{\text{Rhom_A7}} = 0$

The results of this assessment have been verified by comparing calculated isopleths with selected phase equilibrium

data from Braga et al. [5] and Muzaffar [43] as well as with more recent data from Luef et al. [47]. They are shown in Figs. 8–15.

4. The theoretical results and discussion

4.1. Bi–Sn system

Very good agreement was reached between the calculation and experimental phase and thermodynamic data for this system (Figs. 3 and 4). The calculated solubility of the Bi in the BCT_A5 (Sn) solid solution agreed with the results of SEM measurements and the phase boundaries confirmed by the DTA measurements. The eutectic temperature obtained in the calculation is 138.4 °C, which is in very good agreement with the value measured by Braga et al. [5] (138.6 °C). For

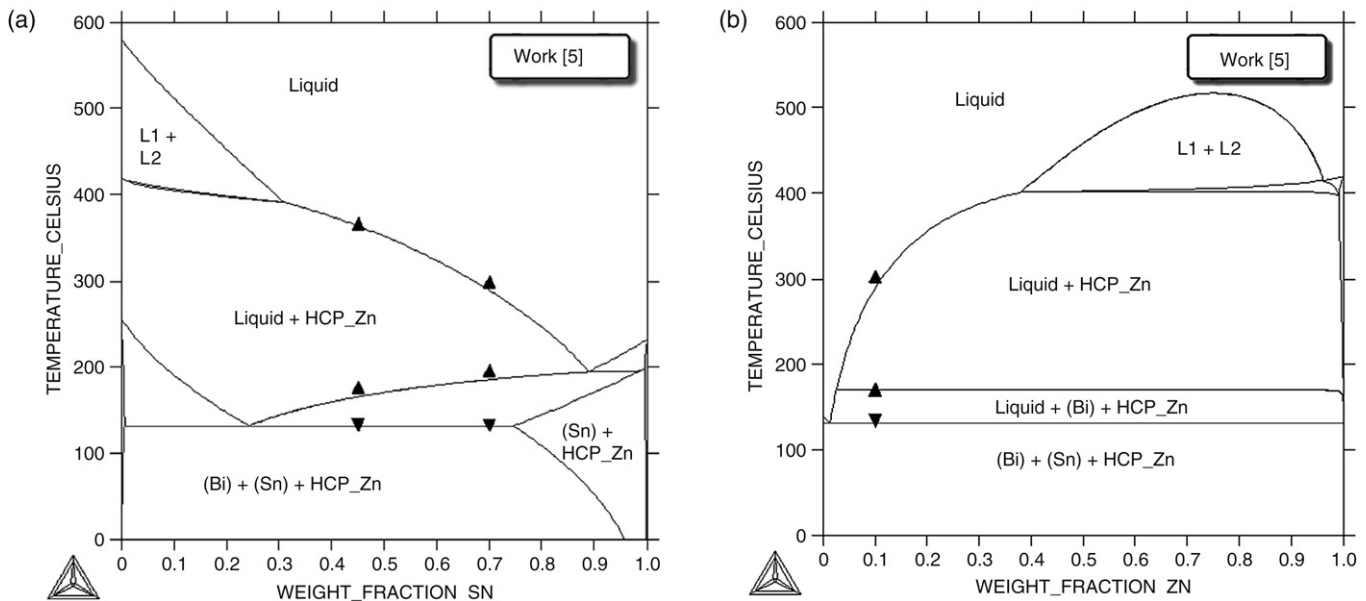


Fig. 10. Calculated vertical sections at constant ratios (a) $W(\text{Bi})/W(\text{Zn}) = 1/2$ and (b) $W(\text{Bi})/W(\text{Sn}) = 2$ in comparison with experimental data from Braga et al. [5].

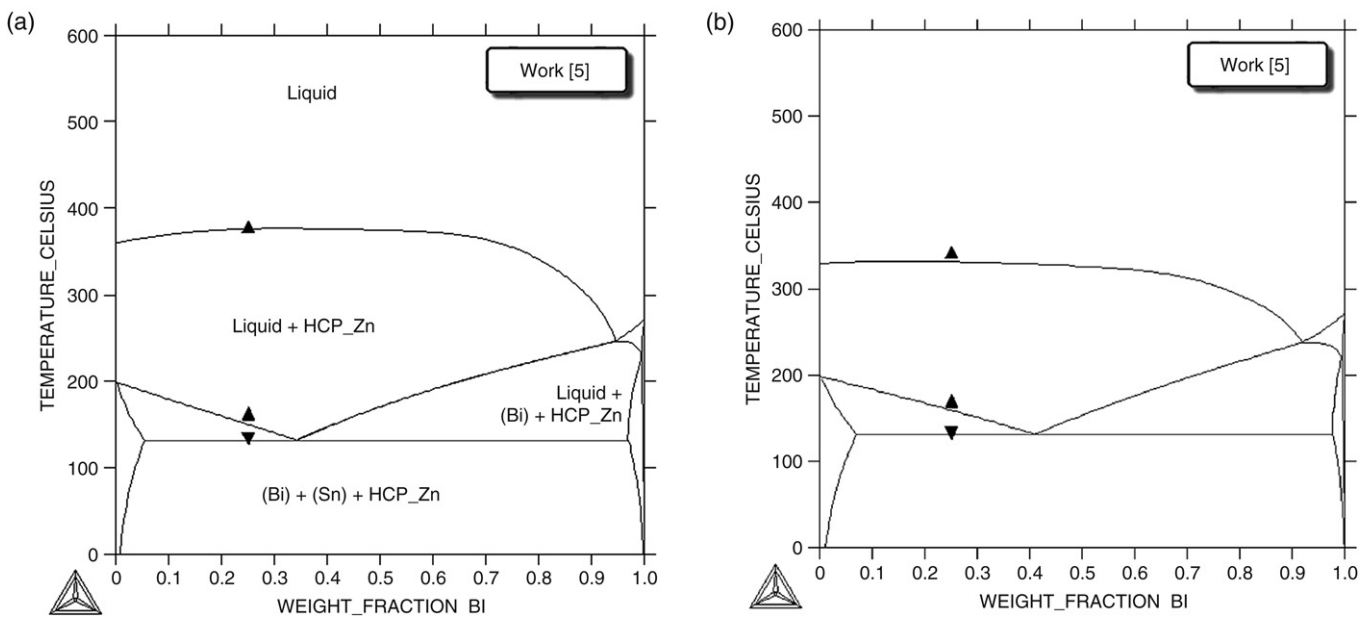


Fig. 11. Calculated vertical sections at constant ratios (a) $W(\text{Sn})/W(\text{Zn}) = 1$ and (b) $W(\text{Sn})/W(\text{Zn}) = 2$ in comparison with experimental data from Braga et al. [5].

comparison, Ohtani and Ishida [10] calculated the eutectic temperature to be 140.7 °C and Lee et al. [19] determined a value of 138.8 °C. A very good agreement between calculated and experimentally measured [15] activities of Sn in liquid Bi–Sn alloys at 450 °C is shown in Fig. 4(a).

The reliability of the new Bi–Sn description was also verified by calculations of the ternary Bi–Sn–Zn system (see Sections 3.5 and 4.3).

4.2. Bi–Zn system

It is clear from the experimental results that the estimated phase boundary [30] in the Bi-rich region is not correct

and that the theoretically calculated solubility of Zn in Rhombohedral A7 (Bi) solid solution using the data from the work of Malakhov [21] is more accurate. The calculated solubility of Bi in HCP_Zn, based on the current reassessment of the relevant interaction parameter, agrees well with experiment; the temperatures and composition of the phases in the invariant reactions are almost unchanged. Further improvement can be achieved by introducing a parameter for temperature dependence, but owing to a lack of experimental data and the spread in the experimentally determined values of the eutectic temperature given in the literature, this would be inappropriate.

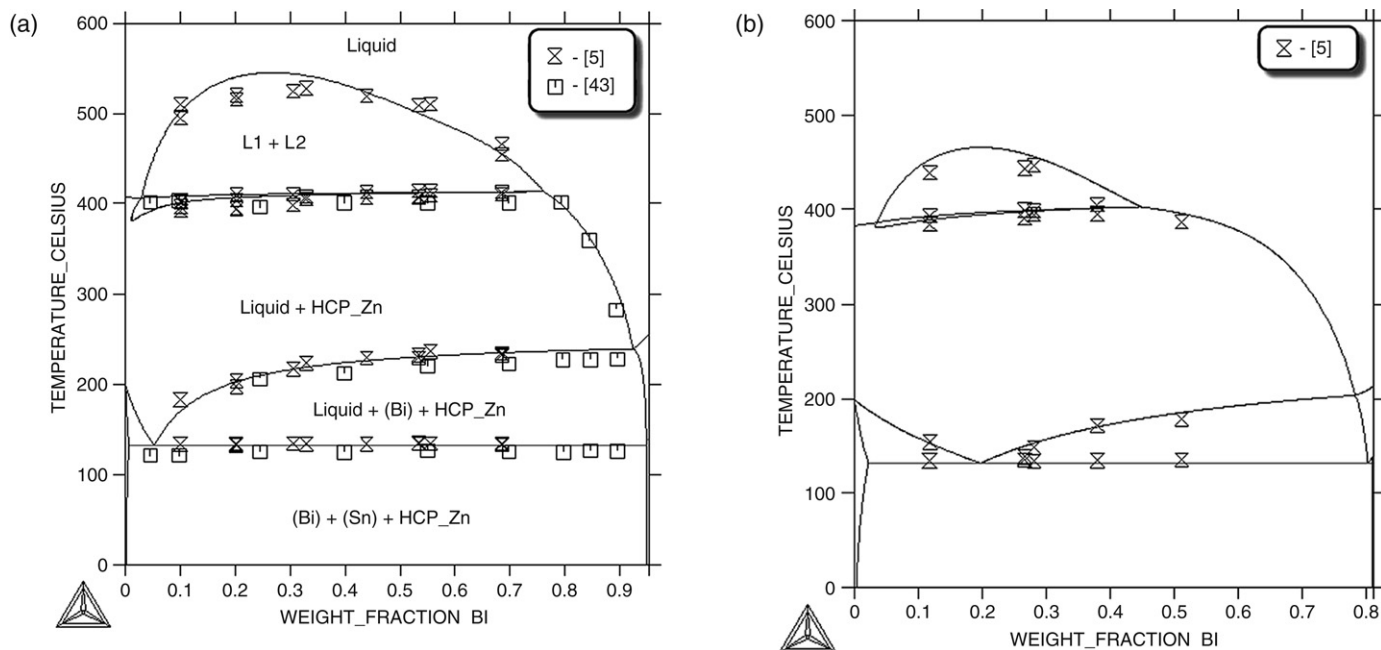


Fig. 12. Calculated vertical sections at (a) 5 wt% of Sn, compared with the experimental data of Braga et al. [5] and Muzaffar [43], and (b) 19 wt% of Sn, compared with experimental data from Braga et al. [5].

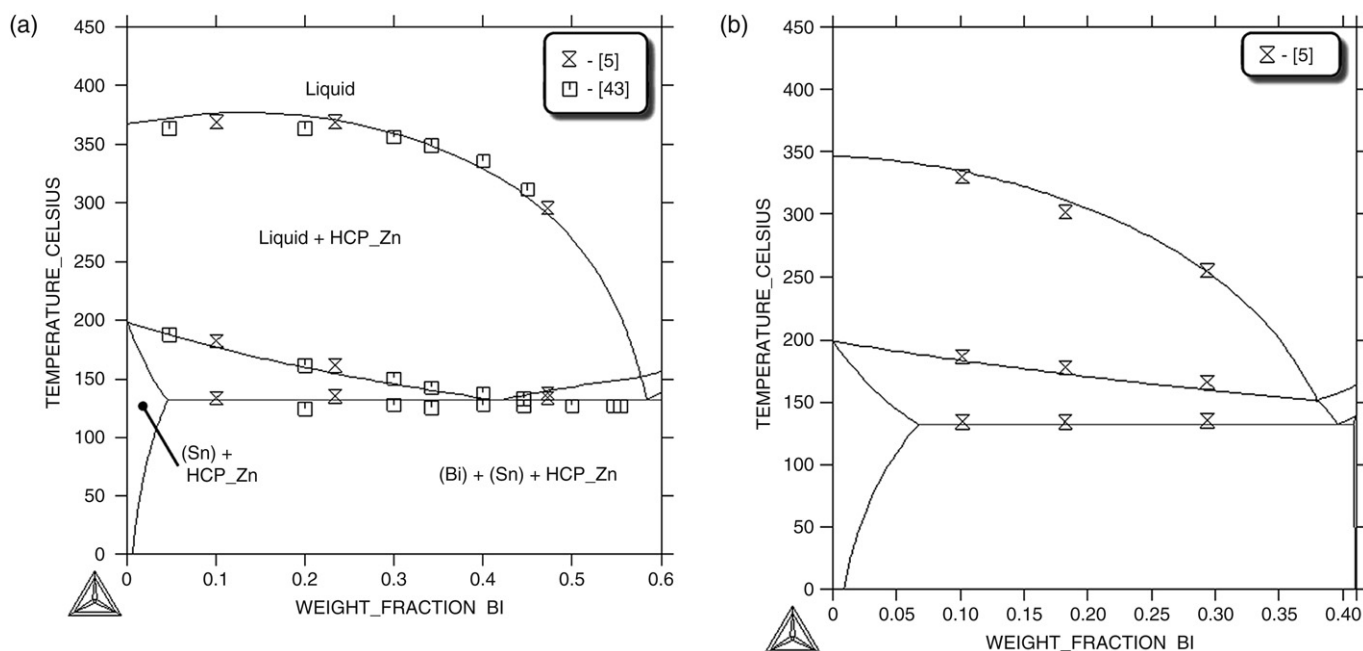


Fig. 13. Calculated vertical sections at (a) 40 wt% of Sn, compared with the experimental data of Braga et al. [5] and Muzaffar [43], and (b) 59 wt% of Sn, compared with the experimental data of Braga et al. [5].

4.3. Bi–Sn–Zn system

The experimentally measured thermodynamic properties and phase equilibria are very well reproduced using the new thermodynamic description in Figs. 8–15. The calculated integral enthalpies of mixing and activities of Zn are compared with experimental data in Fig. 8 (a) and (b), and the agreement is very good.

Fig. 9(a) and (b) show the calculated isothermal sections at 100 and 120 °C, which are in very good agreement with the

experimental data [5]. The agreement between the modeling and experimental data (DTA results) from [5] and [43] is also shown in the relevant vertical sections in Figs. 10–14. It should be noted that smaller weight was given to the experimental data of Muzaffar [43] in comparison with the data of Braga et al. [5] in this assessment. The phase equilibrium data from [5] were given priority in the optimization owing to their reliability and consistency. Muzaffar's thermal analysis results are slightly different (e.g. the temperature of invariant reaction), but the

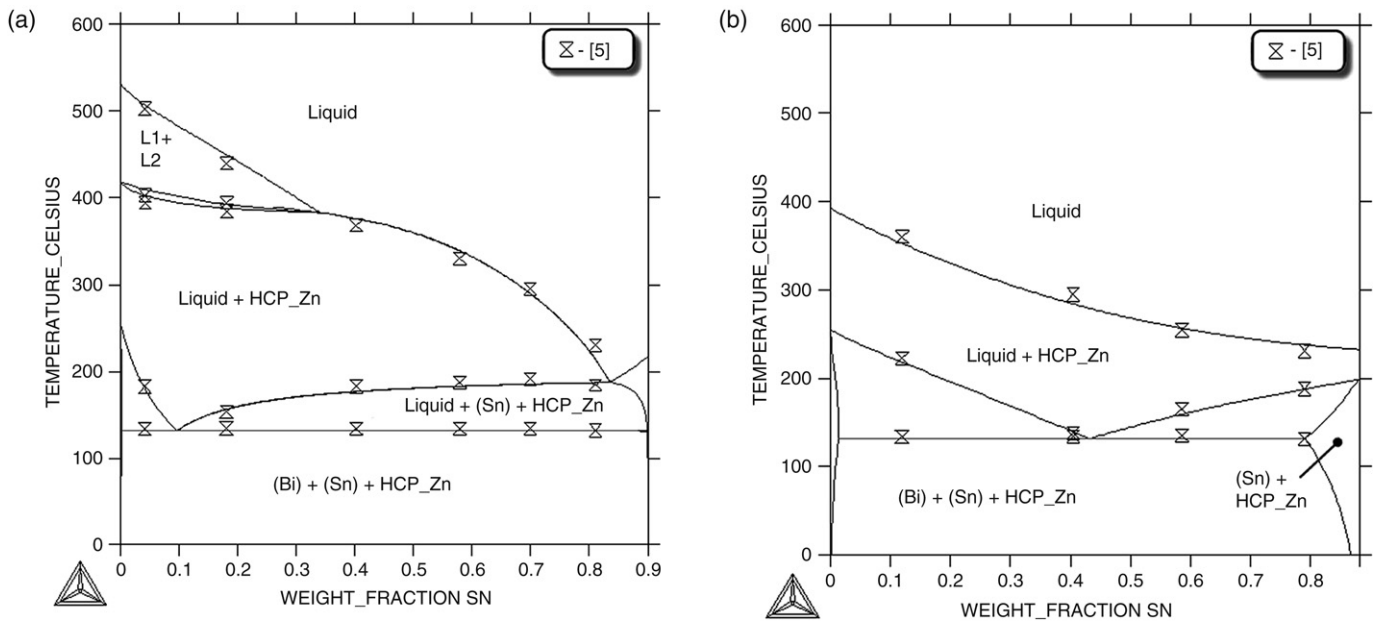


Fig. 14. Calculated vertical sections at (a) 10 wt% of Bi and (b) 12 wt% of Zn, compared with the experimental data of Braga et al. [5].

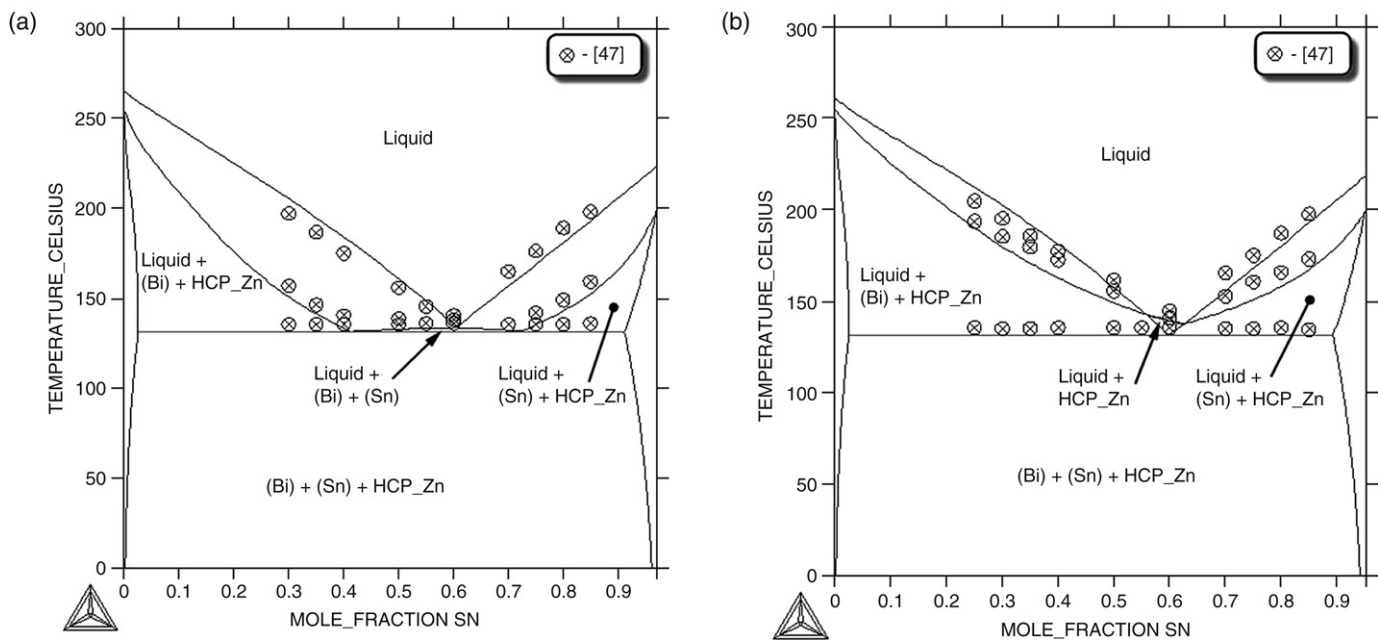


Fig. 15. Calculated vertical sections at (a) 3 at.% of Zn and (b) 5 at.% of Zn, compared with the experimental data of Luef et al. [47].

results are still in reasonable agreement with more recent work. The data of Muzaffar are also very useful because of the number of alloys studied (104!). These alloys covered a major part of the ternary diagram. The ternary eutectic temperature from the work of Muzaffar [43] is 129.87 ± 0.15 °C, but Braga et al. [5] determined this temperature to be 134.1 ± 0.5 °C [5]. The calculated ternary eutectic temperature is 131.7 °C.

We also obtained very good agreement between the calculations and recent experimental results taken from [47] for selected vertical sections. This comparison is shown in Fig. 15.

5. Conclusions

A critical evaluation of the thermodynamic parameters and experimental data available in the literature was carried out for the Bi–Sn, Bi–Zn, Sn–Zn and Bi–Sn–Zn systems.

Our own experimental results [5] led to the verification of the Bi-rich part of the Bi–Zn phase diagram and to a reassessment of the interaction parameter for the HCP_Zn phase in the Zn-rich corner.

In the case of the Bi–Sn system, attention was focused on the Sn-rich part of the diagram, where a different solubility of

Bi in the BCT_{A5} (Sn) phase was found in [5] (approximately 10 wt%), and the system was successfully reassessed.

Using the new Bi–Sn system description, the modification of the Bi–Zn system description and the available thermodynamic and phase equilibrium data, the Bi–Sn–Zn ternary system was also completely reassessed.

The reliability of the assessed parameters obtained for the Bi–Sn–Zn system was verified by calculation of thermodynamic properties and isothermal and vertical sections of the phase diagram. These results were compared with experimental data, both from our work [5] and the literature [43, 45, 47]. The agreement is excellent for a broad set of experimental measurements carried out by different authors. Therefore, the new datasets for the Bi–Sn and Bi–Sn–Zn systems and the modification of the parameter for the Bi–Zn system were included in the “COST531” database [2].

This database, containing 11 elements (Ag, Au, **Bi**, Cu, In, Ni, Pb, Pd, Sb, **Sn** and **Zn**) was created recently in the scope of the COST 531 project [2]. The reliability of the data in this database is validated both by the modeling of thermodynamic properties of the studied systems (e.g. enthalpies of mixing and their comparison with the experimentally measured data) and by the comparison of theoretical and experimental phase equilibrium data, as shown in this paper.

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